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PROJECT ADMINISTRATION DATA SHEET

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Project No. E-18-624 Q5055-3A0 GT/GIT DATE 6 / 9 / 86

Project Director: Dr. Miraslav I. Marek School/~~XXX~~ Materials Engineering

Sponsor: DHHS/PHS/NIH/NIDR

Type Agreement: Grant No. 5 R01 DE03601-13

Award Period: From 7/1/86 To 9/30/87 (Performance) 9/30/87 (Reports)

Sponsor Amount:	This Change	Total to Date
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Title: Effect of Corrosion on Dental Amalgams

ADMINISTRATIVE DATA — OCA Contact E. Faith Gleason

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Defense Priority Rating: N/A — Military Security Classification: N/A

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RESTRICTIONS

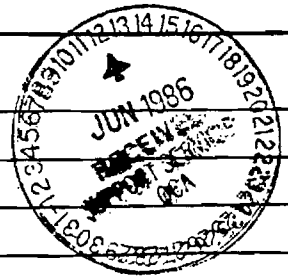
See Attached NIH Supplemental Information Sheet for Additional Requirements.

Travel: Foreign travel must have prior approval – Contact OCA in each case. Domestic travel requires sponsor approval where total will exceed greater of $500 or 125% of approved proposal budget category.

Equipment: Title vests with GIT

COMMENTS:

No cost-sharing required
Continuation of E-18-611



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SPONSORED PROJECT TERMINATION/CLOSEOUT SHEET

Date 3/16/88

Project No. E-18-624 School/~~Lab~~ Material Engrg

Includes Subproject No.(s) N/A

Project Director(s) M. I. Marek GIT ~~GTRC/GIT~~

Sponsor DHHS/PHS/NIH

Title Effects of Corrosion on Dental Amalgams

Effective Completion Date: 9/30/87 (Performance) 9/30/87 (Reports)

Grant/Contract Closeout Actions Remaining:

[X] None

[ ] Final Invoice or Copy of Last Invoice Serving as Final

[ ] Release and Assignment

[ ] Final Report of Inventions and/or Subcontract: Already submitted.
Patent and Subcontract Questionnaire sent to Project Director [ ]

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Continues Project No. E-18-611 Continued by Project No.

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Final Report

EFFECT OF CORROSION ON DENTAL AMALGAMS

By:
Miroslav Marek, Ph. D.
School of Materials Engineering

Under:
Grant No. DE03601
DHHS/PHS/NIH/NIDR

Period of Performance:
06/01/73 - 09/30/87

December 30, 1987

GEORGIA INSTITUTE OF TECHNOLOGY
A UNIT OF THE UNIVERSITY SYSTEM OF GEORGIA
SCHOOL OF MATERIALS ENGINEERING
ATLANTA, GEORGIA 30332

1987

EFFECT OF CORROSION ON DENTAL AMALGAMS

by

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Atlanta, GA 30332-0245

December 30, 1987

FINAL REPORT

Grant No. DE03601
DHHS/PHS/NIH/NIDR

Period of Performance:
06/01/73 - 09/30/87

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I. PROJECT HISTORY

The project was initiated in June, 1973 as a Special Dental Research Award DE03601 under the title "Localized Corrosion of Dental Amalgam" for the budget period 06/01/73 through 05/31/76 (DE03601-01/03). In 1976 a Research Grant with the same title was awarded for the budget period 06/01/76 through 05/31/79 (DE03601-04/06). The title was changed effective the 6th year to "Effect of Localized Corrosion on Dental Amalgams." In 1979 the grant was renewed for the budget period 07/01/79 through 06/30/83 under the title "Effect of Corrosion on Dental Amalgams" (DE03601-07/09).

In 1983 the application for grant renewal for years 10-12 was approved but not funded, and the project period was extended at no cost to 06/30/84 (DE03601-10). A revised application was approved in 1984 and an award made for the budget period 07/01/84 through 06/30/87 (DE03601-11/13). A no cost extension was requested and approved through 09/30/87, when the grant expired.

II. STATUS OF KNOWLEDGE OF CORROSION OF DENTAL AMALGAM AT THE TIME OF PROJECT INITIATION

At the time the project was initiated in 1973 corrosion had been recognized as a major form of deterioration of dental amalgam restorations. Based on the pioneering work of Schoonover and Souder (1), Wagner (2), Jorgensen (3) and others it was known that corrosion of dental amalgam in the oral environment could result in the loss of strength, and that the corrosion most susceptible phase of the dental amalgam structure was the tin-mercury compounds, identified as the gamma-2 phase.

Since the very beginning of serious research of corrosion of dental amalgam it was also recognized that the process was electrochemical, and electrochemical techniques were used to study it. Potentiostatic polarization techniques were used in early studies by, among others, Carter *et al.* (4), Guthrow *et al.* (5) and Lee (6) to establish the basic corrosion characteristics. Mueller *et al.* (7) reported the potential-time behavior. Lee (6) used the linear polarization technique to determine the corrosion rate of dental amalgam in synthetic electrolytes. Other investigators reported results of corrosion product analyses (8), which complemented the electrochemical studies.

Although corrosion was thought to be able to undermine the strength of dental amalgam restorations severely enough to cause bulk fracture (1), the main attention became focused on the fracture of restoration margins, which was identified as the most common major form of failure. From the corrosion viewpoint the significant consideration was that the loss of strength could play an important role in the margin fracture, and that corrosion at the restoration margins, in the crevice between the tooth and the amalgam, could be in the form of localized attack at an accelerated rate. The cause of this acceleration was identified by

Jorgensen (3) to be an oxygen concentration cell, commonly called "differential aeration."

At this state of knowledge of corrosion of dental amalgam there were also many unknowns and some inconsistencies in the scientific evidence. Ignoring the early studies that showed indications of passivity (9), corrosion of the gamma-2 phase was believed to be an active form of dissolution (5). The corrosion roles of the various phases of the dental amalgam structure had not been fully determined. The acceleration of corrosion in the crevice between the tooth and the restoration was attributed to differences in the oxygen concentration only (3), without a recognition of the importance of other local solution chemistry changes. Little was known about corrosion of high-copper amalgams, whichwere showing improved properties and performance over the conventional, low-copper amalgams. The effects of mechanical forces, involved in mastication, on corrosion had not been determined. Galvanic interactions between dental amalgam and other restorative materials had been only superficially explored. Corrosion testing of dental amalgam was performed in many different synthetic electrolytes without sufficient appreciation of the importance of the components. There was no simple corrosion test that could be used to rank commercial or experimental dental amalgams with respect to their corrosion susceptibility.

III. PROJECT OVERVIEW

The project described in this report was undertaken to answer some of the questions regarding corrosion of dental amalgam, as described in the previous section. The significance of the studies was in the possibly major role of corrosion in the failure of dental amalgam restorations, as indicated by substantial early evidence. To evaluate this role thoroughly and contribute to the development of materials with improved properties it was necessary to characterize and explain the corrosion behavior of various amalgams, to study the role of environmental, compositional and structural variables, to document the effects of corrosion on strength and other mechanical properties, and to develop necessary testing procedures. These tasks became the general objectives of the overall study. The specific designs were developed on the basis of the results being obtained and modified as other researchers reported their important contributions to the field, but the overall approach remained the same throughout the duration of the project. Consequently, the studies performed can be summarized as follows:

A. Studies of the Mechanism of Corrosion of Dental Amalgam.

B. Studies of the Effects of Internal and External Variables on Corrosion of Dental Amalgam.

C. Studies of the Influence of Mechanical Effects on Corrosion of Dental Amalgam.

D. Studies of the Effects of Corrosion on Mechanical Properties of Dental Amalgam.

E. Studies of the Galvanic Interactions Involving Dental Amalgam.

F. Studies of Corrosion Testing Techniques.

These studies are described in more detail, but in a summarized form in the next section.

IV. STUDIES PERFORMED

A. STUDIES OF THE MECHANISM OF CORROSION OF DENTAL AMALGAM.

1. Studies of the Fundamental Electrode Behavior of Dental Amalgam.

At the initiation of this project it was generally believed that the most corrosion-prone phase of the dental amalgam structure, the tin-mercury gamma-2 phase, suffers general dissolution, mainly on the basis of the study reported by Guthrow et al. (5). There were some indications that passivity played a role in the behavior of dental amalgam (4,9), but these were mostly ignored.

In the initial studies of this project it was conclusively demonstrated that in saliva (synthetic as well as human) dental amalgam exhibits a substantial region of passivity, which ends when the potential reaches a critical (breakdown) potential. The conflicting evidence of the studies of Guthrow et al. (5) and some other researchers was explained by their failure to deaerate the test solutions, allowing the reduction of dissolved oxygen to mask the evidence of passivity.

In more detailed studies of the electrode behavior of the individual phases of dental amalgam structure it was determined that the electrode behavior was dominated by the electrode characteristics of the tin-mercury gamma-2 phase, which showed the same passivity and breakdown characteristics as dental amalgam. Scanning electron micrographs were obtained which showed conclusively that the corrosion attack on the gamma-2 phase was in the form of pitting, and not uniform dissolution in the active state. It was also observed that in an open-circuit exposure in synthetic saliva, and in the absence of crevices, the gamma-2 phase in the amalgam structure remained protected by a passive film and did not suffer severe corrosion. When polarized beyond the

breakdown potential, and in acidified solutions, the gamma-2 phase was selectively attack and disappeared from the structure, in agreement with the results of examination of corroded dental amalgam restorations.

The corrosion behavior of the silver-tin matrix phase (gamma-1) of dental amalgams also was examined. It was found that while a pure silver-mercury compound suffered little corrosion damage in the oral environment, the presence of tin in the structure, which had been found by electron microprobe analysis (10), made the phase somewhat susceptible to corrosion. Some pitting, and substantial attack at grain boundaries were observed. Almost no attack was observed on the unreacted phases Ag_3Sn and Cu_3Sn.

A study of the corrosion behavior of high-copper dental amalgams showed higher corrosion resistance than that exhibited by low-copper amalgams. In the absence of the tin-mercury gamma-2 phase the phase that was most readily attacked was the reaction phase Cu_6Sn_5. Another study was initiated to investigate the corrosion behavior of this copper-tin phase. Specimens of pure Cu6Sn5 phase were prepared at the Medical College of Georgia, which participated in the study. Examination of the electrode behavior of the Cu6Sn5 phase showed high corrosion resistance, in conflict with the evidence of corrosion deterioration of that phase in high-copper amalgams. The discrepancy was explained in further tests which showed that in the presence of small amounts of mercury the corrosion susceptibility of the Cu6Sn5 phase sharply increased. Specimens of the Cu6Sn5 phase plated with mercury showed behavior consistent with the corrosion behavior of high-copper dental amalgam. In the amalgam mercury is supplied by diffusion from the silver-mercury matrix phase.

Publications and Presentations

Marek, M. and Hochman, R.F., "The Corrosion Behavior of Dental Amalgam Phases as a Function of Tin Content," 51st Session of the IADR, Washington, D.C., 1973.

Marek, M., Okabe, T., and Hochman, R.F., "In vitro Corrosion of Dental Amalgam Phases," General Session of the AADR, New York, 1975.

Marek, M. and Hochman, R.F., "Corrosion Properties of a Low Silver, High Copper Dental Amalgam," 54th Session of the IADR, Miami Beach, 1976.

Marek, M., Hochman, R.F., and Okabe, T., "In vitro Corrosion of Dental Amalgam Phases," J. Biomed. Mater. Res., vol. 10, pp. 789-804, 1976.

Marek, M. and Okabe, T., "Corrosion Behavior of Structural Phases in High Copper Dental Amalgam," 55th Session of the IADR, Coppenhagen, Denmark, 1977.

Fairhurst, C.W., Marek, M., Butts, M.B., and Okabe, T., "New Information on Dispersalloy Corrosion," General Session of the AADR, Las Vegas, 1977.

Marek, M. and Okabe, T., "Corrosion Behavior of Structural Phases in High Copper Dental Amalgam," J. Biomed. Mater. Res., vol. 12, pp. 857-866, 1978.

Marek, M., Okabe, T., Butts, M.B., and Fairhurst, C.W., "Corrosion of the n' (Cu-Sn) Phase in Dental Amalgam," 60th General Session of the IADR, New Orleans, 1982.

Marek, M., Okabe, T., Butts, M.B., and Fairhurst, C.W., "Corrosion of the n'(Cu-Sn) Phase in Dental Amalgam," J. Biomed. Mater. Res., vol. 17, pp. 921-929, 1983.

2. Studies of Localized Forms of Corrosion of Dental Amalgam

Conditions for crevice corrosion exist in the gap between a dental amalgam restoration and the tooth wall, between adjacent restorations or a restoration and the adjacent tooth, in pores of the dental amalgam structure, under the gingiva in restorations having a subgingival portion, and under any incomplete layers covering the surface of the restoration. The existence of a corrosion cell in the marginal crevice was recognized by Jorgensen (3), and that under plaque by Fraunhofer and Staheli (11). These cells

were considered to be forms of an oxygen concentration cell in which the localization of corrosion was due only to the depletion of oxygen at the occluded part of the surface, which made this surface an anode with respect to the cathodic surface where dissolved oxygen was present in the electrolyte.

In a series of studies which were a part of this project it was demonstrated that the main factor accelerating corrosion in the occluded cell were acidification resulting from the hydrolysis of dissolved tin ions, and an increase in the concentration of chloride ions which moved into the crevice to preserve electrical neutrality. The difference in the oxygen concentration merely intensified the attack. Acidity as low as pH 1.5 was experimentally observed, accompanied by sharp increases in concentration of chlorides. Monitoring of the current flow showed that the onset of a high current flowing between the occluded surfaces and the external parts of the cell coincided with the increase in acidity. Polarization studies using a solution simulating that existing in the occluded cell showed that dental amalgam lost the protection of the passive film in this electrolyte.

As a result of these studies it was possible to describe in sufficient detail the mechanism of acceleration of corrosion in various forms of crevice-type cells in dental amalgam. Conditions caused by corrosion in the marginal crevice, especially the high acidity, were such that some tooth demineralization might occur.

Publications and Presentations

Marek, M., Butler, M.F., and Hochman, R.F., "Crevice Corrosion in Dental Amalgam Restorations," 51st Session of the IADR, Washington, D.C., 1973.

Marek, M. and Hochman, R.F., "A Simulated Crevice Corrosion Experiment for pH and Solution Chemistry Determination," Corrosion, vol. 30, no. 6, pp. 208-210, June 1974.

Marek, M. and Hochman, R.F., "Mechanism of Crevice Corrosion of Dental Amalgam Phases," 53rd Session of the IADR, London , England, 1975.

B. STUDIES OF THE EFFECTS OF INTERNAL AND EXTERNAL VARIABLES ON CORROSION OF DENTAL AMALGAM.

1. A Study of the Effect of the Mercury Content on Corrosion and Creep of Dental Amalgam.

This study was performed in an informal collaboration with Dr. David Mahler and his co-workers at the University of Oregon Health science Center, who performed the creep studies as well some of the corrosion testing. Specimens of commercial high-copper amalgams were prepared with different final mercury contents, and the A.D.A. creep and corrosion susceptibility were determined. It was found that a critical mercury content existed above which both creep and the corrosion susceptibility sharply increased. Because of the subtle differences in the corrosion and creep responses to the changes in composition it was hypothesized that the increase in the corrosion susceptibility resulted mainly from the formation of the gamma-2 phase, while creep was affected even before the gamma-2 phase formation by changes in the mercury and tin concentration at the grain boundaries. The significance of the observed behavior was mainly in relation to the fracture of the restoration margins, since higher mercury content had been reported for the regions along the margins. The results showed that this higher mercury content may, in some amalgams, contribute to the premature fracture of the margins.

2. A Study of the Effect of Porosity on Corrosion of Dental Amalgam.

Dental amalgam restorations contain substantial amounts of voids. A surface-open void (pore) is a form of an occluded cell, in which localized crevice corrosion may be expected to occur. This hypothesis was examined in a study in which specimens of commercial dental amalgams were prepared under conditions that resulted in different amounts of porosity. The porosity was determined by techniques of quantitative metallography. The results confirmed that increasing porosity increased the susceptibility to chloride corrosion. Similarly to the results of the study of the effect of the mercury content the results of this study were related to the conditions along the margins of a restoration, where condensation is less effective, resulting in a higher porosity and higher susceptibility to corrosion.

3. A Study of Sulfide Tarnishing of Dental Amalgam.

Dental amalgams are susceptible to tarnishing in sulfide-containing environments. A study of the electrochemical behavior of dental amalgam in sulfide-containing solutions showed that sulfide tarnishing is an electrochemical process causing the formation of a film of an insoluble, dark metal sulfide on the amalgam surface, resulting in the tarnished appearance. The components of the dental amalgam composition most susceptible to the reactions with sulfides were found to be silver and copper.

4. A Study of the Effect of Sulfide Tarnishing on Chloride Corrosion of Dental Amalgam

Since the tarnishing is due to the formation of a surface film of an insoluble metal sulfide, it was suspected that the layer may affect the electrode behavior in chloride solutions. In this study the amalgam specimens were first exposed to a chloride-free, sulfide-containing solution un-

der controlled electrochemical conditions which allowed to vary the amount of sulfide surface film. The solution was then changed for the standard chloride-containing electrolyte simulating the oral environment. The results showed that the sulfide film provided some protection against the chloride attack which is responsible for the main forms of corrosion deterioration. The results demonstrated, among other things, the complexity of the interaction between the oral environment and a metallic dental restorative material.

Publications and Presentations

Marek, M. and Mahler, D.B., "The Corrosion Susceptibility of a High Copper Amalgam as a Function of the Mercury Content," 57th Session of the IADR, New Orleans, 1979.

Biltoft, P., Hochman, R.F., and Marek, M., "The Effect of Porosity on Corrosion of Dental Amalgam," 59th Session of the IADR, Chicago, 1981.

Mahler, D.B., Adey, J.D., and Marek, M., "Creep and Corrosion of Amalgam," J. Dent. Res., vol. 61, no. 1, pp. 33-35, January 1982.

Marek, M., "An Electrochemical Study of Sulfide Tarnishing of Dental Amalgam," 61st General Session of the IADR, Sydney, Australia, 1983.

Marek, M., "The Effect of Sulfides on Chloride Corrosion of Dental Amalgam," 62nd General Session of the IADR, Dallas, 1984.

C. STUDIES OF THE INFLUENCE OF MECHANICAL EFFECTS ON CORROSION OF DENTAL AMALGAM.

1. A Study of the Effect of Creep Strain on Corrosion of Dental Amalgam.

Corrosion behavior of dental amalgam is strongly affected by the presence of a protective passive film. The film, however, can be mechanically disturbed, in which case corrosion is accelerated. Since dental amalgam under stress at body temperatures exhibits substantial creep deformation, creep strain may break the film and accelerate corrosion.

This hypothesis was tested in this study, in which specimens of several commercial dental amalgams were loaded in tension in a special cell which allowed determination of the electrochemical behavior during creep straining. The results showed substantial acceleration of corrosion due to the creep strain especially for low-copper amalgams, which exhibit relatively high strain rate. The increase in the corrosion rate appeared mainly in the passive region, confirming that it is caused by the breaking of the protective passive film.

2. Studies of the Effect of Abrasion on Corrosion of Dental Amalgam

Another possible cause of mechanical-type acceleration of corrosion is abrasion, which also removes the protective passive film. Abrasion of dental amalgam restorations occurs during mastication or bruxing. For this study a special cell was designed and built in which the amalgam specimen was abraded by a rotating tool with leather-faced pads while immersed in synthetic saliva. Electrochemical tests performed in the presence and absence of abrasion showed a substantial increase in the corrosion activity caused by the abrasion for all amalgams. Moreover, a measurement of the current transients showed that repassivation was relatively slow, indicating that at the normal chewing frequency the corrosion rate would remain continuously near the peak value.

In a clinical study performed by Drs. S. Reese and D. Warfield of the Emory University Dental School in cooperation with the Principal Investigator, dental amalgam specimens were placed in non-functional surfaces of dentures worn by five patients of the Dental School. After exposures ranging from six to fourteen months the specimens were examined for corrosion damage. It was found that the corrosion attack was much less severe than for too-born restorations,

confirming the importance of the acceleration of corrosion by mechanical forces.

Publications and Presentations

Averette, D.F. and Marek, M., "The Effect of Creep Deformation on Corrosion of Dental Amalgam," 60th General Session of the IADR, New Orleans, 1982.

Averette, D.F. and Marek, M., "The Effect of Tensile Strain on Corrosion of Dental Amalgam," J. Dent. Res., vol. 62, no. 7, pp. 842-845, July 1983.

Marek, M., "Acceleration of Corrosion of Dental Amalgam by Abrasion," Annual Session of the AADR, Cincinnati, 1983.

Marek, M. "Acceleration of Corrosion of Dental Amalgam by Abrasion," J. Dent. Res., vol. 63, no. 7, pp. 1010-1013, July 1984.

D. STUDIES OF THE EFFECTS OF CORROSION ON MECHANICAL PROPERTIES OF DENTAL AMALGAM.

1. A Study of the Effect of Corrosion on the Compressive Strength of Dental Amalgams of Different Composition.

In this study specimens of thirteen brands of commercial dental amalgams were exposed to a sodium chloride solution at 37°C for periods up to one year and the changes in the compressive strength were determined. SEM and metallographic examination also was performed, and corrosion products identified. The results showed substantial decrease in strength for low-copper amalgams after the corrosion exposure, reaching as high as 50%. For high-copper amalgams the loss of strength was much lower. The main corrosion products were identified as tin oxides and chlorides, and the appearance of the beta-1 phase of the silver-mercury system was observed on corroded surfaces of the high-copper amalgams.

2. A Study of the Effect of Corrosion on Creep of Dental Amalgam.

This study was performed mainly at the Medical College of Georgia with the participation of the Principal Investigator. The A.D.A creep of corroded and uncorroded specimens of both low-copper and high-copper amalgams was compared, and structural changes were examined. The results showed a decrease in the creep rate as a result of corrosion, and an acceleration of the gamma-1 to beta-1 transformation in the corroded specimens.

Publications and Presentations

Averette, D.F., Hochman, R.F., and Marek, M., "The Effects of Corrosion in vitro on the Structure and Properties of Dental Amalgam," 56th Session of the IADR, Washington, D.C., 1978.

Averette, D.F. and Marek, M., "Creep of the Matrix Phases of Dental Amalgam as a Function of Composition," Annual Session of the AADR, Los Angeles, 1980.

Butts, M.B., Okabe, T., Mitchell, R.J., Marek, M., and Fairhurst, C.W., "Creep of a Corroded High Copper Amalgam," Annual Session of the AADR, Los Angeles, 1980.

E. STUDIES OF THE GALVANIC INTERACTIONS INVOLVING DENTAL AMALGAM.

1. A Study of the Galvanic Interaction between Different Amalgams and between Amalgams and Other Dental Alloys.

Galvanic interactions between low- and high-copper amalgams, and both types of amalgam and other types of dental alloys were studied. The open circuit potential differences were measured, and the currents in the galvanic cells were recorded and integrated to obtain a numerical parameters for the evaluation of the severity of the galvanic interaction. In all the galvanic cells the low-copper amalgam was the anode of the cell and suffered accelerated corrosion. Noble and semi-noble dental alloys caused a more severe galvanic corrosion than base dental alloys. the

results showed clearly that the open circuit potential difference is a poor predictor of the severity of the galvanic interaction.

2. A Study of the Galvanic Interaction under Conditions of Constant and Intermittent Contact.

Galvanic interaction in the oral cavity can occur either continuously, when the dissimilar metals are in a continuous contact, or intermittently when they contact each other repeatedly, e.g., during chewing. The differences in the corrosion consequences of the two modes of galvanic interaction were investigated in this study. It was found that in some galvanic cells the intermittent mode of interaction results in a higher rate of corrosion than a continuous contact. This effect was attributed to the passivation of the anode in the continuous contact mode which decreased the flow of the current to a low value, while an intermittent contact caused repeated events of non-steady state dissolution of the passive film.

Publications and Presentations

Marek, M., "Galvanic Interactions between Dental Amalgam and Other Restorative Materials," Annual Session of the AADR, Los Angeles, 1980.

Marek, M., "Galvanic Corrosion of Restorations under Continuous and Intermittent Contacts," 63rd General Session of the IADR, Las Vegas, 1985.

F. STUDIES OF THE CORROSION TESTING TECHNIQUES.

1. A Corrosion Test for Dental Amalgam.

As a part of this project a corrosion test was designed for ranking of dental amalgams with respect to the corrosion susceptibility. The test was based on constant potential coulometry and the ranking parameter was the total anodic charge passed through 1 cm2 of the amalgam surface in 24 hours, exposed to a 1% sodium chloride solution at 37oC at a

constant potential of 0.0 V (SCE). The test conditions induced measurable corrosion in all commercial amalgams, and in the 24 hour exposure sufficient corrosion attack penetrated into the dental amalgam structure to form localized cells which play and important role in spontaneous corrosion of dental amalgam in the oral environment.

A special cell was designed that allowed the use of standard 4 mm dia. x 8 mm long specimens prepared according to A.D.A. specification No. 1 without any other operation which might affect the corrosion behavior. Although the use of the cell is not mandatory for obtaining consistent results, it makes the testing procedure considerably more routine than other arrangements.

Since the reporting of the proposed test procedure the test has been used by several major manufacturers of alloys for dental amalgam in the development of their products. Recently, the test was subjected to an examination by researchers in Europe and received favorable evaluation (12).

2. A Study of Electrolytes for Corrosion Testing of Dental Alloys

Over the years researchers have used many different electrolytes in the corrosion testing of dental amalgam and other dental alloys. These ranged from simple salt solutions to synthetic saliva of several compositions ranging from simple to very complicated. The formulas for the synthetic salivas were derived from analyses of human saliva; because of the great complexity of the human saliva, however, all the formulas represented much simplified electrolytes. At the same time, little attention was paid to the corrosion significance of the components.

In this study the following components were identified as having the greatest corrosion significance: the chloride and phosphate contents, acidity, and buffering capacity.

The chlorides are the ions mostly responsible for the corrosion attack on dental amalgams and base dental alloys because of their destructive effect on the protective passive films. Phosphates, on the other hand, improve the passive films and thus have a protective effect. Corrosion of most metals is strongly affected by acidity of the electrolyte; thus the synthetic electrolyte should approximate the acidity of human saliva, which is efficiently buffered near the neutral value by bicarbonates, carbon dioxide, phosphates and proteins. In occluded corrosion cells, such as crevices and pores, an increase in acidity is the most important part of the mechanism of the accelerated attack. The more strongly buffered is the electrolyte the more it resists this acidification and the less corrosive it is, of other factors are equal. Therefore, the buffering capacity is another parameter of substantial corrosion significance.

In this study the most commonly used electrolytes used in corrosion testing of dental alloys were compared with respect to the above four parameters of corrosion significance. The chloride and phosphate contents, were compared with published data for human saliva. Acidity and buffering capacity were measured and also compared with published data for human saliva. In addition, the redox potential was determined. It was found that none of the electrolytes approximated human saliva well enough without modification. The formula proposed by Tani and Zucchi (13) was found to be both simple and close to human saliva with respect to the above parameters, except for a low phosphate content. A modified formula, with an increased phosphate content and rounded-up amounts of components was proposed for corrosion testing of dental alloys.

Publications and Presentations

Marek, M., "A Corrosion Test for Dental Amalgam," General Session of the AADR, Las Vegas, 1977.

Marek, M., "In vitro Measurement of the Corrosion Resistance of Dental Amalgam," 11th international Biomaterials Symposium, Clemson, 1979.

Marek, M. and Topfl, E., "Electrolytes for Corrosion Testing of Dental Alloys," Annual Session of the AADR, Washington, D.C., 1986.

V. OTHER PUBLICATIONS AND PRESENTATIONS

In addition to the reports of the specific studies listed above, several publications and invited presentation at national and international meetings were based solely or partially on the work performed in this project. These publications and presentations are listed below:

A. Publications

Marek, M., "Corrosion of Dental Materials," in Aqueous Corrosion and Passive Films, pages 331-394, (J.C. Scully, Ed.), London: Academic Press (1983).

Marek, M. "Corrosion in a Biological Environment," International Workshop on Biocompatibility, Toxicity, and Hypersensitivity to Alloy Systems Used in Dentistry, University of Michigan, Ann Arbor, MI, June 24-28, 1985. University of Michigan Press, 1986, pages 103-122.

Marek, M. "An Electrochemical Test for the Evaluation of Sulfide Tarnishing of Dental Alloys," Corrosion and Degradation of Implant Materials: Second International Symposium, ASTM STP 859 (A.C. Fraker and C.D. Griffin. Eds.), pp. 168-178, ASM, Philadelphia, 1985.

Marek, M., "Corrosion of Dental Materials," in Encyclopedia of Materials Science and Engineering, (M.B. Bever, Ed.), pages 896-901, Pergamon Press (1986).

B. Invited Presentations

Marek, M., "Electrochemical Studies of Dental Amalgam," 152nd Meeting of the Electrochemical Society, Atlanta, 1978.

Marek, M. "Corrosion, Galvanic Cell Production, and Release of Metal Ions," Workshop on Biocompatibility of Metals in Dentistry, sponsored by NIH and hosted by ADA, Chicago, IL, July 11-13, 1984.

Marek, M. "Corrosion Testing of Dental Materials," International Conference on Oral Metallic Interactions, Callaway Gardens, GA, October, 1984.

VI. SUMMARY AND CONCLUDING COMMENTS

During the period of this project a substantial progress has been made in the understanding of the various aspects of corrosion of dental amalgam restorations, and this program has made a significant contribution to this knowledge. The studies have shown that corrosion of dental amalgam occurs mainly when the passive film, in the chlorides-containing oral environment, breaks down on the most susceptible phases, *i.e.*, the tin-mercury phase in low-copper amalgams, and the copper-tin phase Cu_6Sn_5 in high-copper amalgams. This breakdown occurs mostly in crevices, pores, under plaque, and in other forms of occluded cells, in which the corrosion reactions result in local solution chemistry changes, especially acidification, an increase in chloride ion concentration, and depletion in dissolved oxygen. In this electrolyte the passive film becomes unstable and corrosion of the susceptible phases is rapid. The passive film also can be mechanically disturbed by strain or abrasion, resulting in corrosion acceleration, *e.g.*, on the occlusal surfaces.

Several corrosion factors have been identified which contribute to the fracture of the restoration margins. The crevice between the tooth and the restoration causes acceleration of corrosion, which is also intensified by the higher porosity and higher mercury content at the margins, and straining during mastication. The accelerated corrosion attack results in the loss of mechanical strength in the marginal regions, so that fracture is facilitated. The observed decrease in creep after corrosion lowers the ability of the material to relax the stresses by plastic deformation and thus may further contribute to the susceptibility to fracture.

Corrosion of the amalgam restorations can be accelerated by a galvanic contact with other dental alloys,

including amalgams of different composition. Sulfide tarnishing, while causing deterioration of appearance, seems to provide some protection against chloride corrosion.

Both chloride corrosion and sulfide deterioration are electrochemical processes and electrochemical techniques are well suited for investigations of the fundamental reactions and effects of variables. Tests based on electrochemical measurements have been found useful in the evaluation of the relative susceptibility of various amalgams to corrosion.

In spite of the considerable depth of understanding of corrosion of dental amalgam, some aspects remain which have not been fully clarified. The corrosion attack in low-copper amalgams seems to be well understood; in these amalgams the susceptible gamma-2 phase is often associated with porosity and may form an interconnected network, explaining the observed easy penetration of the selective attack into the structure of the amalgam. In the high-copper amalgam, in which the susceptible copper-tin phase does not form a network and is not associated with porosity, the penetration of the corrosion attack has not been adequately explained. The contribution of corrosion to the mechanical fracture, although well understood in the general outline of the process and in qualitative terms, should be described in more detail and quantitatively. The corrosion significance of the many components of the complex oral environment have not been adequately investigated. Dental amalgam will remain a major dental restorative material in the foreseeable future, and a better understanding of its deterioration in the oral cavity will contribute to a better quality of dental care.

VII. REFERENCES CITED IN THE TEXT

1. Schoonover, I.C. and Souder, W. J. Am. dent. Ass. 28, 1278-1291 (1941).

2. Wagner, E. Dt. Zahnarztl. Z. 17, 99-106 (1962).

3. Jorgensen, K.D. Acta odontol. Scand. 23, 347-389 (1965).

4. Carter, D.A., Ross, T.K., and Smith, D.C. Br. Corros. J. 2, 199-205 (1967).

5. Guthrow, C.E., Johnson, L.B., and Lawless, K.R. J. dent. Res. 46, 1372-1381 (1967).

6. Lee, L.H. "Corrosion and Electrochemical Characteristics of dental Amalgam." Ph.D. Dissertaion, RPI, Troy, N.Y (1969).

7. Mueller, H.J., Greener, E.H., and Crimmins, D.S. J. Biomed. Mater. Res. 2, 95-119 (1968).

8. Mateer, R.S. and Reitz, C.D. J. dent. Res. 49, 399-407 (1970).

9. Brecht-Bergen, N. and Loebich, O. Dt. Zahnarztl. Wschr. 37, 502-507 (1934).

10. Mahler, D.B., Adey, J.D., and Van Eysden, J. J. dent. Res. 54, 218-226 (1975).

11. Fraunhofer, J.A. and Staheli, P.J. Br. dent. J. 130, 522-524 (1971).

12. Meyer, J-M., Jaecklin, A.P., and Tremblay, D. IADR-Continental European Division 24th Annual Meeting, Paper No. 106 (1987).

13. Tani, G. and Zucchi, F. Minerva Stomat. 16, 710-713 (1967).